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Rapid Determination Method for 12 Pyrethroid Pesticide Residues in Tea by Stir Bar Sorptive Extraction-Thermal Desorption-Gas Chromatography*

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Abstract

The 12 pyrethroid Pesticides residues in tea samples can be rapidly extracted and separated by a noval stir bar sorptive extraction(SBSE)-thermal desorption(TDU)-gas chromatography(GC) method. Impurities and pyrethroid pesticides residues of tea can be seperated by this method.and then use TDU-GC to analyse pyrethroid Pesticides residues. The residues of 12 pyrethroid pesticides at same time can be identified and quantified simultaneously by SBSE-TDU-GC rapidiy with high sensitivity and good reproducibility. This method is simple, rapid, and the average adding standard recovery ratios were 92.89%-105.01%.The correlation coefficient of pyrethroid pesticides in tea samples is ≥0.9926. Good repeatability(n=6) was obtained in all the cases with The relative standard deviation lower 9.7%.Pyrethroid pesticides residues in 4 real tea samples can be determined rapidly by this method, their pyrethroid pesticide residues are all less than MRL of China and European union.

Keywords: pyrethroid pesticide; tea; stir bar sorptive extraction(SBSE); thermal desorption; GC-ECD

European union issued a number of maximum residue limits (MRL) of pesticides in food standard on August 27th 2004. This standard specifies l68 MRL criterion of pesticides in tea items, including some pyrethroid pesticides. Pyrethroids are a class of synthetic esters ,which are derived by changing the chemical structure of natural pyrethrins. Its insecticidal toxicity is increased by 10 to 100 times than the older generation of pesticides(1). Pyrethroids are toxic organic pollutants, which have caused widespread concerned in the international, and some of them have carcinogenic, teratogenic and mutagenic effects. The traditional analysis procedure for
pyrethroid pesticide residues in tea has some problems, such as complicated sample pretreatment, using a large number of organic solvents and so on(2-5). To this end, it is very necessary to work up a multi-residue analytical method with high efficiency, high sensitivity and strong selectivity. In this paper, the pyrethroid pesticide residues in tea would be determined by stir bar sorptive extraction(SBSE) method. Stir bar sorptive extraction(SBSE) is Constituted by the stir bar coated with Poly-dimethyl-siloxane (PDMS)(6). The principles of SBSE and solid phase micro extraction (SPME) are same, but the

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difference between them is that SBSE has a 10 mm-long stir bar coated with 25μL PDMS (Twister, Gerstel) instead of the SPME's polymer coated fibers. So the SBSE has a better solute-extract capability to water samples, and it could be possible to achieve complete extraction if the Ko /w of solute is more than 500. Compared with SPME, SBSE has a much smaller Phase Ratio (aqueous phase volume divided by PDMS volume), so SBSE could obtain a higher extraction recovery than the SPME. Currently, the SBSE is used to determine volatile and semi-volatile organic compounds, including pesticide residues in different samples(7-13). The volume of extraction phase of this method is generally in the range of 55-250 μL. And compared with solvent extraction technology, solid phase extraction technology, supercritical extraction technology, SBSE-TDU technology could obtain a higher concentration factor, more effective separation. At present, the technology has been successfully applied to the analysis of environmental samples, contaminants and pesticide residues in food and the biological samples, which is very promising solvent-free sample handling technique. [1]

1. Materials and Methods

1.1 Instruments and Reagents

Use Agilent6890N Gas Chromatograph with CIS-4 inlet; TDU desorption system (Germany Gerstel); SBSE solid phase micro extraction stir bar (10 mm × 0.5 mm, 25 μL PDMS, Germany Gerstel); use high pure helium for carrier gas; ECD detector; HP-5 (30 m × 0.32 mm × 0.25 μm) chromatographic column; magnetic stirrer; vial (20 mL).

Methanol (chromatographic pure), deionized water.

Standard solution of pyrethroids: fenson, allethrin, Ovex, tetramethrin, fenpropathrin, permethrin,cypermethrin, deltamethrin, fenvalerate, bifenthrin, cyfluthrin. The mass concentration is 100 mg/L, all of these standard solution were purchased from The Environmental Protection Research Test Institute of Ministry of Agriculture of China and The Standard Sample Research Center of China.

1.2 Instrument Conditions

Thermal desorption conditions (TDU): splitless injection mode; from 20 ℃ to 300 ℃ with 60℃/min rate (to keep 30min); the temperature of transmission line is 350 ℃; the conditions of cold injection system CIS-4: solvent vent mode, from 0 ℃ to 300 ℃ with 12 ℃/s rate (to keep 5 min).

GC conditions: column temperature is from 70 ℃ (to keep 2min) to 220 ℃ with 15 ℃/min rate, with 2 ℃/min rate rose to 270 ℃, with 5 ℃/min rate rose to 290 ℃ (to keep 3min); the carrier gas is nitrogen.

1.3 Sample Handling and Analysis

It is necessary to make conditions standardized before the initial use of stir bar. Placing a stir bar in an empty thermal desorption tube and heat it for 4 h at 300 ℃.Setting CIS-4 temperature at 290 ℃, and keeping 30min. Nitrogen flow is 1mL/min. The stir bar should have aging experiment after using 5 to 6 times, with the same conditions as above.

Weighing 2.000g sample in the flask after the crushed tea sample been over 425 μm sieve, adding 8mL methanol then making ultrasonic extraction for 15 min. Putting 2 mL top of the methanol extracts to a 20 mL headspace vial, adding 18mL distilled water and stirring the solution with 1000 r/min rate for 1 h. After the extraction is completed, remove the stir bar and rinse it with a small amount of distilled water. Finally

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2. Results and Analysis

2.1 Influence Factors of the Extraction Efficiency

2.1.1 Extraction Time

Under the same experimental conditions (certain rotor speed and extraction temperature), adding 4 μL mixed standard solution (fenson, allethrin, Ovex, tetramethrin, fenpropathrin, permethrin,cypermethrin, deltamethrin, fenvalerate, bifenthrin, cyfluthrin are in the concentration of 2μg/L) into six 20 mL headspace bottles which were added with 20 mL pure water already. Then in different extraction time (0.25, 0.5, 1, 2, 4, 8 h), comparing the extraction efficiency according to the chromatographic peak area (peak area of each pyrethroid is the sum of all of its isomers' peak area)of 12 pyrethroids. The results indicated that the total peak area of 12 pyrethroids were increased with increase of the extraction time. The extraction was not reached equilibrium in 8 h, but when the extraction time was 1 h, peak area growth rate slowed down. And the peak area got a fastest growing in the range of 0 - 1 h. In order to achieve the purpose of rapid determination, the best extraction time was designated as 1h.

2.1.2 The Influence of Methanol on Extraction Efficiency

As the tea samples is solid, it can not be extracted directly. So before the sorption extraction, methanol extraction was implemented, and then the samples of methanol extraction was extracted by stir bar sorptive extraction(SBSE) method after diluted by distilled water. Methanol in extraction diluted with distilled water may have effects on the coefficient of recovery of Aimed Compound, so methanol extraction was replaced with methanol to investigate the effects of volume fraction of methanol (0, 10%, 20%, 40% and 60%) on extraction volume. The results showed that the methanol from 0-20% can strengthen stir bar to target extraction. But when the volume fraction range from 40% to 60%, stir bar to target extraction of Aimed Compound was weakened. The reason may be that the additional methanol reduce the adsorption of compound by Vial wall, but the High concentrations of methanol make PDMS have effect on The adsorption of compound. When volume fraction of methanol was added from 0 to 10%, Peak area almost Compounds was augmented largely. In order to save solvent, the methanol whose volume fraction was 10% has been used in this experiment. That is to say, 2 mL of methanol extraction was diluted with distilled water before Pretreatment with SBSE.

2.2 Optimization of Conditions of Thermal Desorption

At the same conditions of SBSE, Desorption temperature, Desorption time and CIS-4 inlet temperature of cold trap influence the thermal desorption Aimed Compound from Stirring rod and entrance into Capillary column.

2.2.1 Optimization of Desorption Time

With the desorption time range from 20 to 40min, the total peak area was increased, which was because that The longer thermal desorption time lead the More volatilization of organic on Stirring rod. in view of the slow increase of peak area when the desorption time range from 20 to 40min, 30min of desorption time was used to control the Experimental time in this Experiment.

2.2.2 Optimization of Desorption Temperature

With the desorption temperature range from 250 to 300℃, the total peak area of all pyrethroids were increased, which was because that the higher desorption temperature lead more volatilization of organic compound. 300℃ desorption temperature was used in this Experiment.

2.2.3 Optimization of CIS-4 Inlet Temperature of Cold Trap

With the CIS-4 inlet temperature range from 0℃ to below zero, The total peak area was reduced in turn. 0℃ of CIS-4 inlet temperature was used in this experiment.

The results showed that 300℃ desorption temperature, 30min of desorption time and 0℃ inlet temperature of cold trap were the best conditions.

2.3 Evaluation of Method

Using standard addition method, use blank sample added with guide sample to quantify, to eliminate the of sample matrix.in this experiment, Mixed standard solution whose concentration range from 0.3-3 μg/ml and 8 ml of methanol were added to 2 g blank tea sample after ultrasonic extraction for 30 min, 2ml of Upper liquid was moved to 20 ml vial added by 18 ml of purified water for Stir bar sorptive extraction. The extraction time and methanol concentration were 1h and 10%. The experiment was been repeated for 6 times to Measure peak area and make standard curve under the best conditions. Correlation coefficient, relative standard deviation and recoveries were showed in Table 1.Analysis results meet the requirements of pesticide residues analysis.

Table 1 Correlation coefficient ,relative standard deviation, recoveries

Pyrethroid	Linea-rities	RSD (n=6,%)	Recoveries (n=6,%)
Fenson	0.9935	5.2	95.37
Allethrin	0.9926	9.7	92.89
Ovex	0.9928	5.1	105..01
Tetramethrin Fenpropathrin	0.9991	5.1	101.13
Permethrin	0.9942	5.5	96.57
Trans-cypermethrin	0.9937	5.6	104.06
Cis-cypermethrin	0.9969	7.6	101.16
Deltamethrin	0.9986	7.6	99.26
Fenvalerate	0.9953	9.5	97.06
Bifenthrin	0.9970	3.6	97.20
Cyfluthrin	0.9996	5.1	104.48
	0.9980	3.0	101.04

2.4 Analysis of Real Samples

4 tea samples purchased at random were detected for 3 Parallels using the above methods. Average were showed in Table 2. The results show that pyrethroid residues in tea samples did not exceed the stringent limits made by China and the EU(14-15).

Table 2 Pyrethroid Pesticides in Tea Samples ($\mu g \cdot kg^{-1}$)

Pyrethroid	Pu'er Tea	DaFang Tea	Jasmine Tea	Jasmine Beads Tea
Fenson	—	0.0798	—	—
Allethrin	0.0403	—	—	—
Ovex	—	—	—	—
Tetramethrin	—	—	0.0901	—
Fenpropathrin	—	—	—	0.05243
Permethrin	—	—	0.0806	—
Trans-cypermethrin	—	0.0975	—	—
Cis-cypermethrin	—	—	—	0.5383
Deltamethrin	—	—	—	—
Fenvalerate	0.0409	—	—	—
Bifenthrin	—	—	—	—
Cyfluthrin	—	—	—	—

Note: — means less than detection limit.

3. Conclusion

This study established a new method which use SBSE-TDU-GC to detect the pyrethroid pesticides in tea, and the correlation coefficient(≥0.9926),The relative standard deviation(≤9.7, n=6) and recovery ratio(92.89%-105.01%) reached the testing requirements of pyrethroid in tea. The method have some virtues such as relatively simple pretreatment, short processing time and good repeatability. Besides, the method was applicable to pyrethroid pesticide residue detection requirements of tea. SBSE-TDU-GC rapid determination may be used in detection of other food pesticide widely in the future. on the other hand, in order to get optimum results of specific components in specific sample, More appropriate methods and testing conditions should be established.

As can be seen from the experimental results, Cypermethrin, permethrin and tetramethrin residues detected in 4 tea samples were relatively more, which means that the use of these types of pesticides in teaplantation should be noticed. Pyrethroid residues in tea samples of China did not exceed the stringent limits made by China and the EU.

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